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WASTES INTO PRODUCTION

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RECYCLING WASTES FROM OZOKERITE PRODUCTION IN LARGE-TONNAGE ENERGY-CONSERVING TECHNOLOGY FOR FABRICATING CONSTRUCTION CERAMIC

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A comprehensive study of the wastes from ozokerite production at the Borislavskoe deposit (L'vov oblast', Ukraine) was performed. It was determined on the basis of data from x-ray phase, differential thermal and petrographic analyses as well as from the determination of the main physical and ceramic properties of the wastes and compositions in combination with additives such as secondary kaolin from the Murzinskoe deposit, primary alkaline kaolin from the Dubrovskoe deposit and fly ash from the Ladyzhinskaya TPP that these wastes can be used effectively in the batch to obtain construction ceramic. Introducing the wastes into the batch makes it possible to reduce their sensitivity to drying, intensify the molding process and reduce the consumption of the main heat carrier during firing.

Key words: ozokerite, construction ceramic, firing, water absorption, mechanical strength, plasticizer, sintering, plastic molding.

Mineral wax is a naturally occurring polymer material associated with oil-bearing rock and coal. It is obtained by extraction from the ore body, which contains materials such as sandstone and shale as impurities, using hot water or substances (benzene) that dissolve the main material (ozokerite) [1]. Depending on the natural conditions of formation the ores can contain up to 40—45% of the indicated and other associated minerals and, therefore, after the desired material has been extracted large quantities of wastes are formed and, as a rule, must be stored as tailings. For this reason it is important to study the possibility of using the wastes from the production of ozokerite in large-tonnage technologies, including ceramic technology.

In the present work we studied wastes from the production of mineral wax, thousands of metric tons of which have accumulated after enrichment of ozokerite ore from the Borislavskoe deposit (L'vov oblast').

The clayey mass studied in the dried state is dark gray and possesses a layered texture in the form of large, easily comminuted aggregates which soak poorly in water.

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The experimental clayey materials can be classed as clay shale on the basis of their morphological properties [2]. Distinct diffraction peaks are practically entirely absent in the x-ray diffraction patterns of the materials studied (Fig. 1), and the intensity of the peaks that are present is no more than 70 – 75 counts/sec, so that one cannot talk about the presence of crystalline formations, well-formed by natural erosion processes, in the material studied.

The reflections that are identified attest to the presence of hydromica (illite), muscovite, calcite and â-quartz in the materials studied. The hydromica consists of products of different degrees of hydration of micas and occupy an intermediate position between micas and montmorillonites [3], so that they are evidently difficult to identify in the x-ray diffraction pattern. However, it can be supposed that being in a finely disperse state with a disordered structure the materials studied will manifest high activity and make it possible to sinter articles.

Differential-thermal analysis of the wastes studied showed (Fig. 2) that endo- and exothermal effects associated with the following physical and chemical processes are observed in the DTA curve with increasing temperature.

The endo effect at 130°C is associated with the removal of hydroscopic and adsorption water from argillite [2]. A se-

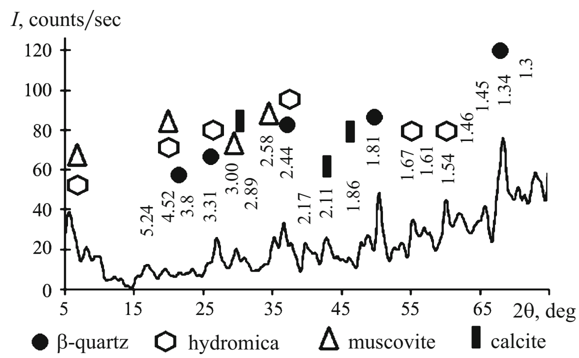

Fig. 1. X-ray diffraction pattern of wastes from the production of ozokerite.

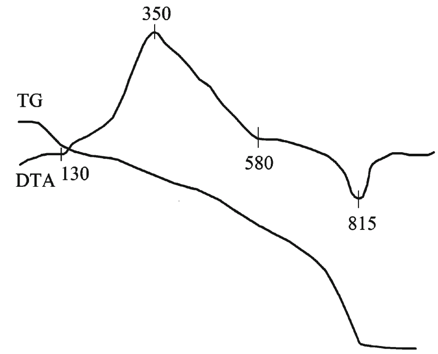

Fig. 2. Derivatogram for the wastes from the production of ozokerite.

cond endothermal effect at 580°C is associated with dehydration where constitution water is removed from the structure of clayey minerals. In addition, this endo effect can also be associated with modification transformations of quartz [4]. A third endo effect peaking at 815°C attests to the final destruction of the hydromica lattice and decomposition of carbonates, as is confirmed by significant mass loss of material recorded by the TG curve. The presence of a very intense exothermal effect at 350°C should be noted. It is associated with the combustion of organic substances present in the wastes being studied, first and foremost, ozokerite residues.

The physical and ceramic properties of the clayey raw material, which make it possible to predict the possibility of using it in different fields, were determined in the course of the present investigations. For this the experimental samples were comminuted to full passage through a No. 08 sieve, wetted to a plastic dough with normal working moisture content, allowed to age in order to smooth the moisture content over the entire volume and for the clayey particles to swell more completely. Cubic samples with the dimensions 30×30 mm were molded from the plastic body obtained, dried under natural conditions to moisture content 5 – 7% and fired at temperatures 1000 and 1100°C.

During the drying process, even under the sparing conditions indicated above, many cracks appeared on the samples, which shows that the clayey materials studied are highly sensitive to drying. The results of the determination of the physical and mechanical properties of the raw materials studied are presented in Table 1.

It was found that the linear dimensions of the samples changed very little after firing and the increase in the water

TABLE 1. Physical and Mechanical Properties of Wastes from the Production of Mineral Wax

Air shrinkage, %	Firing temperature, °C	Flame shrinkage, %	Total shrinkage, %	Water absorption, %	Strength in compression, MPa	Other
7.5	1000	0.50	7.50	18.70	18.6	14.65
	1100	2.27	9.32	14.71	30.9	16.54

absorption to 18.70% attests to the presence of gas-forming compounds and burnable impurities in the raw material. The high mechanical strength of the samples in compression (18,6 MPa) attests to the formation of a quite dense structure. Sintering is more complete at 1100°C according to the values of the fire shrinkage (2.27%) and mechanical strength (30.9 MPa) and the samples have a cream brick color.

According to the data presented the products of enrichment of ozokerite could be of interest as auxiliary raw material for the production of construction ceramic. The sandstone in them plays the role of a leaning additive, which determines the relatively high shrinkage of the samples (7.50 – 9.32% in the temperature interval 1000 – 1100°C), while the shale (after fine milling) has a plasticizing effect, which parts plasticity and improves the molding properties of the body [2]. In addition, the mechanical strength of the samples even after firing at 1000°C corresponds to ceramic brick grade at least M 150 [5].

The presence of significant amounts of residual ozorite can play a very important role in this material. Burning up in the process of firing articles and releasing internal heat it makes it possible to conserve the consumption of the external heat carrier and impart uniformity to firing as well as to obtain high-strength articles by means of energy-conserving technology.

In summary, when studying the wastes from the production of mineral wax it was found that they could be suitable for preparing ceramic construction materials with firing in the temperature interval 1000 – 1100°C. However, considering the high sensitivity of the wastes being studied to drying modifying additives that would make it possible to decrease this index must be sought.

At the next stage of the investigations the following were chosen as readily available additives in clayey wastes from the enrichment of mineral wax: ferruginizated secondary kaolin from the Murzinskoe deposit (MK-3), primary alkaline kaolin from the Dubrovskoe deposit and fly ash from the electric filters at the Ladyzhinskaya TPP.

The simplex-lattice method was used to plan the experiment (Fig. 3). The experimental bodies were prepared by

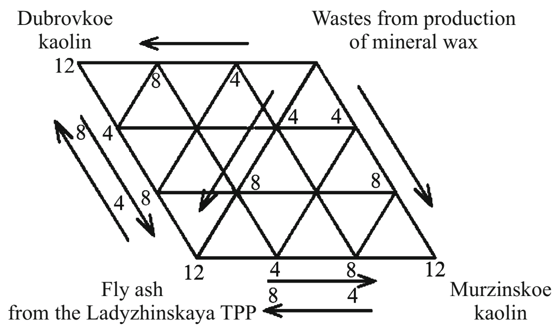

Fig. 3. Simplex-lattice plan of the experiment (the content of the raw materials by weight).

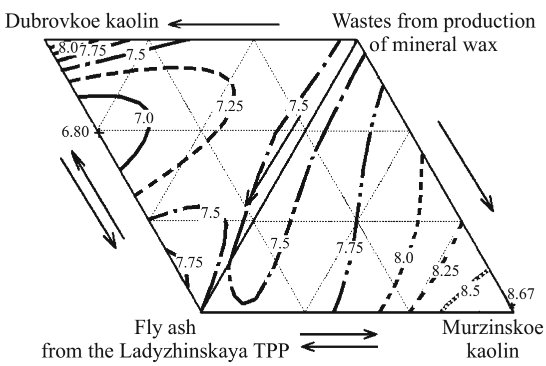

Fig. 4. Total shrinkage (indicated on the curves, %) of the experimental samples versus the amount of additives (firing temperature 1000°C).

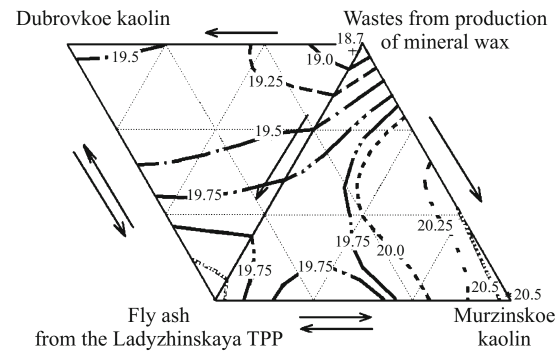

Fig. 5. Water absorption (indicated on the curves, %) of the experimental samples versus the amount of additives (firing temperature 1000°C).

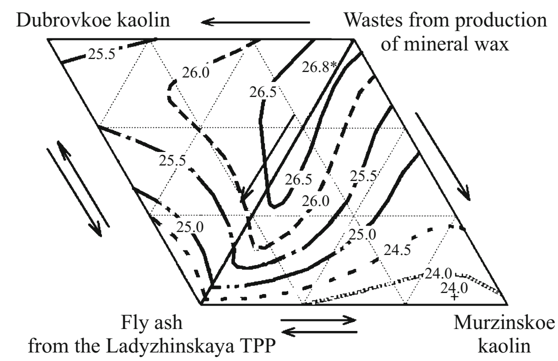

Fig. 6. Mechanical strength of the experimental samples in compression (indicated on the curves, MPa) versus the amount of additives (firing temperature 1000°C).

comminuting the indicated materials to full passage through a No. 08 sieve, weighing in a prescribed ratio (total mass constant 100%) and carefully mixing them. After leaning with water, the working moisture content of the body was 18 – 20%. The cubic samples were molded and dried under natural conditions.

It should be noted that on adding the indicated additives the cohesion of the body decreased very little, but it was adequate for plastic molding of the samples without any visible defects. In addition, the cracks vanished after the samples were dried.

The results of the dependence of the total shrinkage, water absorption and mechanical strength in compression of the experimental samples in compression on their properties are presented in Figs. 4 – 6.

The investigations have shown that after firing at 1000°C the total shrinkage of the ceramic samples into which Murzinskoe kaolin was added to mass fraction 12% increases to 8.67% (compared with 7.5% for the initial samples). This is associated with the elevated shrinkage of kaolinite during its dehydration.

The water absorption of the samples also increases to 20.5% while the mechanical strength in compression decreases to 24.0 MPa (as compared with 18.7% and 26.8 MPa for the base value). This can be explained by a reduction of the sintering intensity [6], since refractory Murzinskoe kaolin is introduced into the ceramic body based on low-melting clayey raw material.

The introduction of fly ash to mass fraction 12% has practically no effect on the shrinkage of the samples (it remains in the range 7.4 – 7.5%), which is a manifestation of its leaning effect — the ash creates a framework in the structure of the samples. However, at the same time the sintering of ceramic bodies is degraded, which is expressed as an increase of the water absorption to 20% and a reduction of the strength to 24.5 MPa.

Alkaline kaolin was added on the assumption that its action is complex, since this kaolin contains kaolinite, quartz, microcline and very small amounts of impurities [7]; in addition, aside from the leaning effect of quartz and kaolinite's effect of expanding the sintering range the feldspar component was expected to have a sintering effect, which the interaction with the low-melting components of the wastes from the enrichment of mineral wax could intensify. However, it turned out that the introduction of Dubrovskoe alkaline kaolin to mass fraction 12% increased the shrinkage of the samples to 8.25%, and in addition the water absorption increased slightly to 19.5% while the mechanical strength decreased to 25.5 MPa. Thus, the addition of alkaline kaolin did not have a sintering effect at the given firing temperature.

The introduction of a complex additive containing (mass fraction) 8% alkaline kaolin and 4% fly ash was most effective in reducing the total shrinkage (6.8%). However, at the same time the water absorption remains high (19.5%) and the mechanical strength low (compared with the base value) at 25.5 MPa.

In summary, it can be concluded that wastes from the enrichment of mineral wax (ozokerite) can be used in the production of construction ceramic as a base as well an additive to other clayey materials. However, some specific features of their properties must be taken into account.

The quite high plasticity of the wastes studied is associated not with the high content of clayey minerals in them but rather with the residue of the ozokerite component, which softens during the molding of the articles (temperature of the bar extending out of the vacuum press is 60 – 70°C), which facilitates the molding process by lubricating the rubbing surfaces of the press, and during firing, where it burns up, thereby decreasing the consumption of the main heat carrier. It is possible that the cracking of the samples during drying is associated with the presence of this same residue.

The results of the investigations also showed that the introduction of such modifying additives as secondary kaolin from the Murzinskoe deposit and fly ash from the Ladyzhenskaya TPP makes it possible reduce the sensitivity of the compositions obtained to drying, but then in all cases the water absorption and mechanical strength of the fired materials degrade somewhat.

On the whole the result of this work have shown that the wastes from the enrichment of mineral wax can be used in compositions of ceramic bodies for the manufacture of construction ceramics as a complex plasticizing additive in combination with low-melting clayey materials will provide completeness and uniformity of sintering at temperatures 1000 – 1100°C.

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